

## Full length article

# Oxygen nonstoichiometry, defect equilibria, and thermodynamic characterization of LaMnO<sub>3</sub> perovskites with Ca/Sr A-site and Al B-site doping

M. Takacs<sup>a</sup>, M. Hoes<sup>a</sup>, M. Caduff<sup>a</sup>, T. Cooper<sup>a</sup>, J.R. Scheffe<sup>b,\*</sup>, A. Steinfeld<sup>a,\*</sup><sup>a</sup> Department of Mechanical and Process Engineering, ETH Zurich, 8092 Zurich, Switzerland<sup>b</sup> Department of Mechanical and Aerospace Engineering, University of Florida, Gainesville, FL 32611-6250, USA

## ARTICLE INFO

## Article history:

Received 24 August 2015

Received in revised form

14 October 2015

Accepted 16 October 2015

Available online xxx

## Keywords:

Solar fuels

Perovskites

Oxygen nonstoichiometry

Thermochemical

Defect chemistry

## ABSTRACT

This work encompasses the thermodynamic characterization of four doped lanthanum manganites, namely La<sub>0.6</sub>A<sub>0.4</sub>Mn<sub>1-y</sub>Al<sub>y</sub>O<sub>3</sub> (A = Ca, Sr and y = 0, 0.4), all showed to be promising redox materials for the solar thermochemical splitting of H<sub>2</sub>O and CO<sub>2</sub> to H<sub>2</sub> and CO. We present oxygen nonstoichiometry measurements in the temperature range  $T = 1573\text{ K}–1773\text{ K}$  and oxygen partial pressure range  $p_{\text{O}_2} = 4.5066 \times 10^{-2}\text{ bar}–9.9 \times 10^{-5}\text{ bar}$ . For a given  $T$  and  $p_{\text{O}_2}$ , oxygen nonstoichiometry is found to be higher when replacing the divalent dopant Sr in La<sub>0.6</sub>Sr<sub>0.4</sub>MnO<sub>3</sub> by the divalent Ca but also increases significantly when additionally doping 40 mol-% Al to the Mn-site. La<sub>0.6</sub>Ca<sub>0.4</sub>Mn<sub>0.6</sub>Al<sub>0.4</sub>O<sub>3</sub> revealed the highest mass specific oxygen release, 0.290 mol O<sub>2</sub> per kg metal oxide at  $T = 1773\text{ K}$  and  $p_{\text{O}_2} = 2.360 \times 10^{-3}\text{ bar}$  and  $0.039\text{ mol kg}^{-1}$  at  $T = 1573\text{ K}$  and  $p_{\text{O}_2} = 4.5066 \times 10^{-2}\text{ bar}$ . It is shown that the chemical defect equilibrium of all four perovskites can be accurately described by the two simultaneous redox couples Mn<sup>4+</sup>/Mn<sup>3+</sup> and Mn<sup>3+</sup>/Mn<sup>2+</sup>. Thermodynamic properties, namely partial molar enthalpy, entropy and Gibbs free energy are consequently extracted from the defect models. Partial molar enthalpy decreases with increasing oxygen nonstoichiometry for the Al-doped perovskites whereas the opposite trend is observed for the others. The enthalpy falls within the range 260–300 kJ mol<sup>-1</sup> for all the materials. Equilibrium hydrogen yields upon oxidation with H<sub>2</sub>O are determined as a function of redox conditions. Although reduction extents of the perovskites are greater compared to CeO<sub>2</sub>, oxidation with H<sub>2</sub>O and CO<sub>2</sub> is thermodynamically less favorable. This leads to lower mass specific fuel productivity compared to CeO<sub>2</sub> under most conditions relevant for solar thermochemical cycles.

© 2015 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

## 1. Introduction

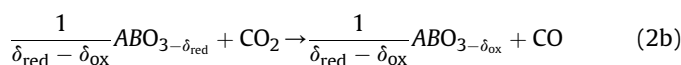
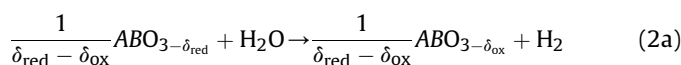
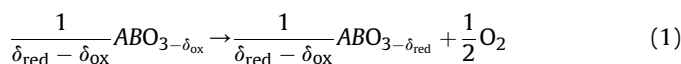
Nonstoichiometric ceria (CeO<sub>2</sub>) is currently considered to be a state-of-the-art redox material for solar-thermochemical splitting of H<sub>2</sub>O and CO<sub>2</sub> to H<sub>2</sub> and CO (syngas) because of its rapid oxidation and reduction kinetics and its morphological stability over a range of temperatures and reduction extents [1]. Compared to other metal oxide systems (e.g. volatile ZnO [2] and non-volatile ferrites [3,4]), ceria shows relatively low fuel productivity per unit mass of metal oxide [5–7]. It has been shown that reduction extents of ceria can be increased by introducing 4+ valence dopants such as Zr<sup>4+</sup> [8–12] and Hf<sup>4+</sup> [8,13] into the ceria lattice. However,

thermodynamic calculations for Zr<sup>4+</sup>-doped ceria [7,12] showed that oxidation with H<sub>2</sub>O is less favorable compared to pure ceria. This results in a lower theoretical solar-to-fuel energy conversion efficiency for Zr<sup>4+</sup>-doped ceria because of larger temperature swings between the redox steps and/or excess oxidant gas [7]. Lower conversion efficiency was also reported for other ceria dopants such as Gd<sup>3+</sup>, Y<sup>3+</sup>, Sm<sup>3+</sup>, Ca<sup>2+</sup> and Sr<sup>2+</sup> [6].

Perovskite oxides have recently been proposed as promising alternative reactive intermediates for solar thermochemical H<sub>2</sub>O/CO<sub>2</sub> splitting because of potentially increasing the energy conversion efficiency by lowering the reduction temperature or increasing the mass specific fuel yield [14–23]. The two-step solar-thermochemical cycle based on a generic perovskite (ABO<sub>3</sub>) is represented by

\* Corresponding authors.

E-mail addresses: [jscheffe@ufl.edu](mailto:jscheffe@ufl.edu) (J.R. Scheffe), [aldo.steinfeld@ethz.ch](mailto:aldo.steinfeld@ethz.ch) (A. Steinfeld).



where Eq. (1) represents the high-temperature endothermic reduction and Eq. (2) the lower temperature exothermic oxidation with H<sub>2</sub>O (a) and CO<sub>2</sub> (b).  $\delta_{\text{red}}$  and  $\delta_{\text{ox}}$  represent the oxygen nonstoichiometry after reduction and oxidation, respectively, whereas the difference  $\delta_{\text{red}} - \delta_{\text{ox}}$  is the molar amount of fuel produced per mole of metal oxide. Scheffe et al. [14] considered strontium-doped lanthanum manganites La<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3</sub> ( $x = 0.30, 0.35, 0.40$ ) and reported reduction extents of La<sub>0.6</sub>Sr<sub>0.4</sub>MnO<sub>3</sub> to be nearly 6.5 times larger than those of ceria at 1600 K and twice larger at 1800 K, both for  $p_{\text{O}_2} = 10^{-5}$  bar. However, it was shown that their theoretical solar-to-fuel energy conversion efficiency is lower compared to that of ceria because of the thermodynamically less favorable oxidation with CO<sub>2</sub> and H<sub>2</sub>O. Based on measurements of Mizusaki et al. [15], Yang et al. [16] concluded higher reduction extents and, consequently, higher fuel yields with increasing  $x$  for La<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3</sub> ( $0 \leq x \leq 0.5$ ), while H<sub>2</sub>O-to-H<sub>2</sub> conversion rate decreased with increasing  $x$ . This led to the conclusion that intermediate doping levels may be optimal for solar-to-fuel energy conversion. McDaniel et al. [17] showed even higher CO and H<sub>2</sub> yields when additionally doping Al to the B-site of La<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3</sub> while maintaining fast oxidation rates with CO<sub>2</sub> and H<sub>2</sub>O. Dey et al. [18] showed increasing reduction extents and fuel productivity when replacing the divalent A-site dopant Sr in La<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3</sub> with Ca and obtained best results for  $x = 0.5$ . In another recent work [19], they investigated two series of perovskite oxides, Ln<sub>0.5</sub>Sr<sub>0.5</sub>MnO<sub>3</sub> and Ln<sub>0.5</sub>Ca<sub>0.5</sub>MnO<sub>3</sub> (Ln = La, Nd, Sm, Gd, Dy, and Y) and concluded highest O<sub>2</sub> release for the manganite with the smallest A-site cation radius (in this case Y). A comparison between La<sub>x</sub>Sr<sub>1-x</sub>MO<sub>3</sub> (M = Mn, Co, Fe) and Ba<sub>x</sub>Sr<sub>1-x</sub>(Co,Fe)O<sub>3</sub> [20] showed best results for the Mn-containing perovskites. In a very recent study by Cooper et al. [21], Sr and Ca A-site doped lanthanum-manganites, with and without B-site doping of Al, were examined for redox performance and compared to the state-of-the-art material ceria. La<sub>0.6</sub>Sr<sub>0.4</sub>Mn<sub>0.6</sub>Al<sub>0.4</sub>O<sub>3</sub> and La<sub>0.6</sub>Ca<sub>0.4</sub>Mn<sub>0.6</sub>Al<sub>0.4</sub>O<sub>3</sub> reach four to nine times higher reduction extents compared to ceria in the temperature range  $T = 1473 \text{ K} - 1673 \text{ K}$ , while maintaining fast oxidation kinetics with CO<sub>2</sub>. Bork et al. [22] reported that La<sub>0.6</sub>Sr<sub>0.4</sub>Cr<sub>1-x</sub>Co<sub>x</sub>O<sub>3</sub> with the optimal dopant concentration  $x = 0.2$  can split up to 25 times more CO<sub>2</sub> when cycling at  $T = 1073 \text{ K} - 1473 \text{ K}$  compared to ceria or exhibits similar reduction extents ( $\delta = 0.034$ ) at 300 K lower temperatures (1473 K instead of 1773 K). On the other hand, cyclability redox studies by Galvez et al. [23] revealed that the chemical stability of Ca, Sr and Al-doped La–Mn perovskites is detrimentally affected by sintering and by the formation and eventual segregation of a carbonate phase during oxidation by CO<sub>2</sub>.

Some of the conclusions drawn for the perovskites discussed above are mainly based on qualitative reduction experiments under an inert flow of low  $p_{\text{O}_2}$  and oxidation under a relatively high flow of CO<sub>2</sub> and/or H<sub>2</sub>O in a thermogravimetric analyzer [18–20,22] and/or in an electrically heated furnace coupled to a gas analysis [17,18]. Such experiments with large excess of CO<sub>2</sub> and/or H<sub>2</sub>O can result in misleading conclusions, as indicated by various thermodynamic analyses [14,16,21]. In the work of Yang et al. [16], the amount of H<sub>2</sub>O needed to oxidize La<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3</sub> ( $0 \leq x \leq 0.4$ ) to a certain  $\delta_{\text{ox}}$ ,

and hence produce a fixed amount of H<sub>2</sub> in a closed system with variable volume was calculated from thermodynamic data. Similar calculations were performed by Scheffe et al. [14] and Cooper et al. [21], however, there, the initial amount of CO<sub>2</sub> and/or H<sub>2</sub>O was fixed and the fuel yield was predicted as a function of oxidation temperature. Such thermodynamic fuel yield calculations allow for an accurate determination of the material's potential to efficiently split CO<sub>2</sub> and/or H<sub>2</sub>O.

In this work, we build on the recent work of Cooper et al. [21] and report detailed oxygen nonstoichiometry measurements of La<sub>0.6</sub>A<sub>0.4</sub>Mn<sub>1-y</sub>Al<sub>y</sub>O<sub>3</sub> ( $A = \text{Ca, Sr}$  and  $y = 0, 0.4$ ) over a wide temperature range  $T = 1573 \text{ K} - 1773 \text{ K}$  and oxygen partial pressure range  $p_{\text{O}_2} = 4.5066 \times 10^{-2} \text{ bar} - 9.9 \times 10^{-5} \text{ bar}$ . The refinement of the nonstoichiometry measurements allows the development of more appropriate defect models to describe the defect chemical equilibria and to extract finer trends in partial molar thermodynamic properties ( $\Delta \bar{h}_\text{O}^\circ$ ,  $\Delta \bar{S}_\text{O}^\circ$ ,  $\Delta \bar{G}_\text{O}^\circ$ ). From such data we determine equilibrium hydrogen yields and evaluate the potential of these lanthanum-manganites to be used as reactive intermediates in solar thermochemical redox cycles.

## 2. Experimental section

### 2.1. Sample preparation and characterization

La<sub>0.6</sub>Sr<sub>0.4</sub>MnO<sub>3</sub> (LSM40), La<sub>0.6</sub>Ca<sub>0.4</sub>MnO<sub>3</sub> (LCM40), La<sub>0.6</sub>Sr<sub>0.4</sub>Mn<sub>0.6</sub>Al<sub>0.4</sub>O<sub>3</sub> (LSMA) and La<sub>0.6</sub>Ca<sub>0.4</sub>Mn<sub>0.6</sub>Al<sub>0.4</sub>O<sub>3</sub> (LCMA) perovskite powders were synthesized by sol–gel method as described by Scheffe et al. [8]. The corresponding metal nitrates (see Table 1 in electronic supplementary information<sup>1</sup> (ESI)) and anhydrous citric acid (Sigma–Aldrich, catalog nr. 251275) in aqueous solution were used to carry out the synthesis. The ratio of the metal cations to the citric acid was 1:1.5. The aqueous solution was slowly heated up to 573 K to perform the pyrolysis. Afterwards, powders were calcined at 1273 K under air for 5 h. Dense cylindrical pellets were obtained by uniaxially cold-pressing the powder at 5 tons followed by sintering at 1773 K under air atmosphere for 24 h. The approximate dimensions after sintering were 6.4–6.9 mm diameter and 1–2 mm height and the mass of the pellets was ~250 mg (LSM40), ~290 mg (LCM40), ~150 mg (LSMA) and ~270 mg (LCMA). Dopant concentrations were measured by inductively coupled plasma-atomic emission spectroscopy (ICP-OES) and deviated by less than 4% from their nominal composition for LSMA and LCMA. Powder X-ray diffraction (XRD) was performed in the Bragg Brentano geometry using Cu K $\alpha$  radiation (Philips, PANalytical/X'Pert MPD/DY636,  $\lambda = 1.5406 \text{ \AA}$ ,  $2\theta = 20 - 100^\circ$ ,  $0.01^\circ \text{ s}^{-1}$  scan rate, 45 kV/20 mA output). Scanning electron microscopy (SEM) of the dense pellets was conducted on a TM-1000Microscope (Hitachi, 15 kV accelerating voltage). ICP-OES analysis, XRD patterns and SEM images are shown in ESI.

### 2.2. Thermal analysis

Oxygen nonstoichiometry was measured using a thermogravimetric analyzer (TGA, Setaram Setsys Evolution). Pellets were suspended to the balance with a custom-made platinum hook to ensure good exposure to the purge gas and eliminate gas diffusion limitations. The  $p_{\text{O}_2}$  of the sweep gas was controlled by mixing Ar (Messer, Argon 4.6) with O<sub>2</sub>/Ar mixtures (Messer, 5% O<sub>2</sub> 5.0 in Ar 5.0 and 0.1% O<sub>2</sub> 5.0 in Ar 5.0). Gases were mixed with electronic mass

<sup>1</sup> Electronic supplementary information (ESI) available: List of metal nitrates used for sample preparation, ICP-OES analysis, XRD patterns, SEM images, detailed derivation of defect model and additional results.

Download English Version:

<https://daneshyari.com/en/article/7879566>

Download Persian Version:

<https://daneshyari.com/article/7879566>

[Daneshyari.com](https://daneshyari.com)